

# Electrochemical determination of methyl parathion using poly(malachite green)/graphene nanosheets–nafion composite film-modified glassy carbon electrode

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**Abstract** A novel poly(malachite green)/graphene nanosheets–nafion (PMG/GNs–NF) composite film-modified glassy carbon electrode was developed to indirectly detect methyl parathion (MP). *p*-nitrophenol, the alkaline hydrolysis product of MP, was successfully determined at a relatively lower potential using this modified electrode due to the excellent electrocatalytic activity of PMG/GNs–NF composite film. The presence of GNs in the composite film enhanced the stability of PMG and increased the electron transfer rate. The kinetic parameters of modified electrodes were studied. What is more, the optimum experimental parameters affecting response were selected in terms of pH, accumulation potential, accumulation time, scanning cycles during polymerization of malachite green, and alkaline hydrolysis conditions. Under optimum conditions, the chronoamperometric response current was proportional to MP concentration over the range from 0.02 to 1.5  $\mu\text{M}$  with a low-detection limit of 2.0 nM. Finally, the sensor was applied for the determination of MP in real samples, and the results were satisfactory with recoveries from 97.20 to 104.53 %. Due to its simple preparation, good reproducibility, and stability, this developed modified electrode provides a new platform for the detection of organophosphate pesticides.

**Keywords** Malachite green · Graphene nanosheet · Modified electrodes · Electrocatalysis · Methyl parathion

## 1 Introduction

Organophosphorus pesticides (OPs) have gained great popularity in increasing agricultural productivity because of their extreme toxicity and low cost [1]. However, their extensive use poses a serious risk to environment and human health. The acute toxicity exposing to OPs derives from the fact that they can target vast important proteins, such as acetylcholinesterase (AChE), which is of particular significance for the functions of central and peripheral nervous system. The World Health Organization has classified OPs as “extremely hazardous” for the environment [2]. Hence, it is considerably crucial and necessary to develop a simple, economical, and sensitive analytical method for the determination of OPs.

Traditional analytical approaches, such as liquid or gas chromatography coupled with mass spectrometry [3–5] and high-performance liquid chromatography [6, 7], have high sensitivity, accuracy, and specificity. However, these methods are expensive and laboratory oriented, limiting their use primarily to laboratory settings instead of rapid analysis on online monitoring. Enzyme biosensors have been playing an important role in acting as the most promising alternative for the detection of pesticides in recent years [4, 8]. Especially, the inhibition and non-inhibition biosensors, based on immobilization of AChE or organophosphorus hydrolase (OPH) onto various electrochemical or optical transducers, have emerged for OPs analysis [1, 9–11]. Although high sensitivity can be achieved, these methods suffer from limited stability of enzymes caused by denaturation during immobilization and storage [12].

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As a promising alternative to these approaches, chemically modified electrodes (CMEs) prove to be advantageous in electrocatalysis and sensor development in the past decades, because they can lower overpotential, improve sensitivity and selectivity, and avoid surface fouling [13–15]. Moreover, CMEs have been successfully used for the determination of OPs [16–18]. Some OPs and carbamate pesticides, such as methyl parathion (MP) and carbaryl [19, 20], can be hydrolyzed in alkaline aqueous solution, resulting in the formation of their corresponding phenolic derivatives. Rao et al. [20] improved the carbamate pesticide detection limits by electrochemical detection after hydrolyzed to their corresponding phenolic derivatives. Similarly, electrochemically detecting some OPs using alkaline hydrolysis instead of OPH may be an economical and sensitive method.

Poly(malachite green) (PMG) is generated by electrochemical polymerization of malachite green (MG). MG has an open but ionized structure. Its resulting conjugated polymer PMG, whose redox reaction possibly results from the quinoid structure inside it, holds great promise for catalytic toward small organic molecules [21]. Previous studies have reported the catalytic ability of PMG toward dopamine, ascorbic acid, etc. [22, 23]. Chen et al. [24, 25] used the enhanced electrocatalytic activity of PMG combining with nafion (NF)-multiwalled carbon nanotube to detect phenols and alcohols.

Conjugated polymers combining nanomaterials show good mechanical stability, sensitivity, and electrocatalysis for multiple compounds detection [26]. Among various nanomaterials, graphene nanosheets (GNs) have great attraction as a novel single-atom-thick two-dimensional graphitic carbon electrode material because of their large

surface area, high thermal and electrical conductivities, impressive mechanical properties, and low cost. Their superior qualities have opened the way for potential applications in nanoelectronics [27], sensors [28, 29], nanocomposites [30, 31], catalysis [32], capacitors [33], etc. The sensitivity of the electrochemical signal can be further improved by using GN-based amplifications.

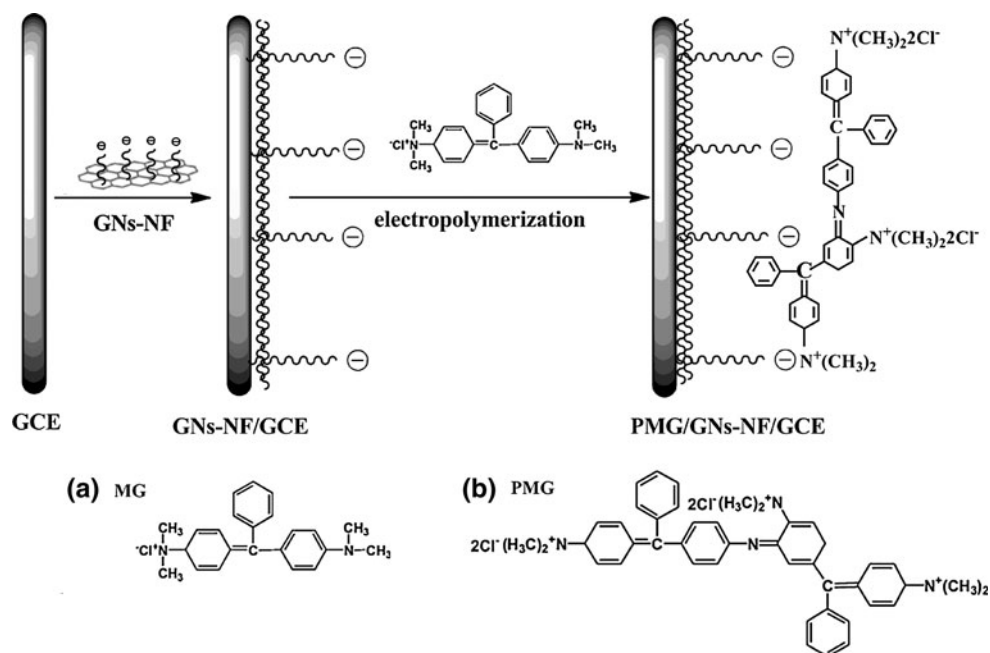
As a typical kind of OPs, MP has been severely restricted in agriculture by the United Nations Environment Programme and the Food and Agricultural Organization [34]. In this study, a new poly(malachite green)/graphene nanosheets–nafion (PMG/GNs–NF) composite film was successfully fabricated to detect MP. Its preparation involved two steps (shown in Scheme 1): (i) electrodes were modified with uniformly well-dispersed GNs–NF (the interaction between GNs and NF is hydrophobic) and (ii) which was then modified with PMG (the interaction between NF and PMG is both hydrophobic and electrostatic). The experimental parameters were investigated, and under the optimum experimental conditions the fabricated electrode was further applied to detect MP by monitoring the electrochemical response of its phenolic derivative after absolute alkaline hydrolysis. The developed sensor gave favorable results, suggesting it paved a new and economical way for the determination of MP.

## 2 Experimental

### 2.1 Reagents and apparatus

Methyl parathion (*O,O*-dimethyl *O*-(4-nitrophenyl) phosphorothioate, MP) and *p*-nitrophenol were purchased from

**Scheme 1** Schematic diagram of the PMG/GNs–NF/GCE preparation



Aladdin Reagent Co. Ltd. (Shanghai, China), and their stock solutions were prepared in anhydrous ethanol.  $1.0 \text{ mg mL}^{-1}$  GNs were prepared with doubly distilled water containing 0.5 % (wt%) NF. Phosphate buffer solution (PBS) was prepared by mixing stock solution of 0.1 M  $\text{NaH}_2\text{PO}_4$  and 0.1 M  $\text{Na}_2\text{HPO}_4$ . MG was obtained from Tianjin Basf Chemical Co., Ltd. (China). 2.5 mM of MG stock solution was prepared by dissolving 228.1 mg of MG into 250 mL of pH 1.5  $\text{H}_2\text{SO}_4$  aqueous solution and stored in refrigerator (4 °C). All other materials were analytical grade, and all the aqueous solutions were prepared with double-distilled water from quartz.

Electrochemical experiments were performed with CHI832A electrochemical workstation (Shanghai Chenhua Co., China) and CHI660C electrochemical workstation (Shanghai Chenhua Co., China) with a conventional three-electrode cell. A bare glassy carbon electrode (GCE) ( $d = 4 \text{ mm}$ ) or a modified GCE was used as working electrode. A saturated calomel electrode and a platinum wire were used as reference electrode and auxiliary electrode, respectively.

## 2.2 Preparation of the GNs

The GNs were synthesized according to the previous report [35]. Briefly, two high-purity graphite rods acting as electrode were immersed into the 3-D water solution of 5.0 M  $\text{KPF}_6$  and with parallel distance of 4.0 cm. The constant current of 0.2 A was used to two graphite rods by WLS-5 model constant current meter (Nanjing, China) for 2 h, then the current was converted to 1.0 A. After 3 h, the exfoliation products were taken out of the reactor and washed thoroughly with water and ethanol, respectively. At last, the products were dried at 60 °C in oven for 6 h.

## 2.3 Fabrication of modified electrodes

Prior to modification, a GCE was carefully polished to a mirror with 0.3 and 0.03  $\mu\text{m}$  alumina powders in sequence, then sonicated in anhydrous ethanol and double-distilled water for 3 min, respectively, finally dried with nitrogen for next modification. The fabrication of PMG/GNs–NF modified electrode involved two steps: first, a polished electrode was uniformly coated with 8  $\mu\text{L}$  well-dispersed GNs–NF solution and dried at room temperature (noted as GNs–NF/GCE). Second, the GNs–NF/GCE was electropolymerized by continuous cyclic voltammograms (CVs) in the potential range from 0 to 1.2 V at a scan rate of  $100 \text{ mV s}^{-1}$  in a pH 1.5  $\text{H}_2\text{SO}_4$  aqueous solution containing 2.5 mM MG (noted as PMG/GNs–NF/GCE). Subsequently, the PMG/GNs–NF/GCE was carefully washed with double-distilled water to remove the loosely attached non-polymerized MG monomer and dried at room temperature. For comparison, the PMG/NF/GCE was also

prepared in the similar procedure. All the modified electrodes were stored at 4 °C before use.

## 2.4 Alkaline hydrolysis and chronoamperometric measurements of MP

The alkaline hydrolysis of MP was performed by adding sodium hydroxide at room temperature, which was then followed by the addition of hydrochloric acid to adjust the pH. The hydrolysis degree of MP was confirmed by UV–Vis. The optimal alkaline hydrolysis conditions including hydrolysis time and the concentration of NaOH were obtained based on the standard curve between *p*-nitrophenol concentration and absorbance. These prehydrolyzed samples were determined at the PMG/GNs–NF/GCE by chronoamperometry in 0.1 M PBS (pH 5.0) with the potential range from 0.3 to 0.45 V.

## 2.5 Real samples analysis

Samples of vegetable and real water were used to value the practicality of this developed sensor, and standard addition method was adopted to estimate the accuracy. Vegetable sample of cabbage was obtained from local market and cleaned using double-distilled water. The pretreatment of the vegetable was on the basis of previous report with modification [36]. Briefly, 1 kg of cabbage was spiked with 5 mg of MP. After overnight, the sample was extracted with 30 mL of absolute ethyl alcohol. The supernatant was taken and filtered through a 0.45- $\mu\text{m}$  membrane then evaporated to dryness. 100 mL of ethanol was added to dissolve the dry residue. In analysis, the samples were determined as detailed in Sect. “2.4”.

# 3 Results and discussion

## 3.1 Surface morphological studies of GNs–NF and PMG/GNs–NF composite films

Figure 1 showed the scanning electron microscopy (SEM) images of GNs–NF and PMG/GNs–NF films on the electrodes. Comparison of Fig. 1a and b displayed significant morphological difference between the two films. It can be seen from Fig. 1a that uniformly dispersed GNs in NF were shown on the GCE surface, and the crumpled structure of GNs was obvious. In Fig. 1b, with the increase in deposition of PMG on GNs–NF film, the PMG/GNs–NF film was more wrinkled compared with GNs–NF film, which could facilitate the increase in surface area and the electron transfer. This phenomenon revealed that the PMG was successfully polymerized on the surface of GNs–NF film.

### 3.2 CVs of different modified electrodes and electrocatalytic oxidation of *p*-nitrophenol

Figure 2a showed the CVs of bare GCE (a), GNs–NF/GCE (b), PMG/NF/GCE (c), and PMG/GNs–NF/GCE in the absence (d) and presence (e) of *p*-nitrophenol in 0.1 M PBS (pH 7.0) at  $100 \text{ mV s}^{-1}$  scan rate in the potential range of 0–0.8 V. Among these modified electrodes, there were no redox couples at bare GCE (a) and GNs–NF/GCE (b), whereas there were redox couples of PMG at NF- and GNs–NF-modified electrodes. Compared with PMG/NF/GCE (c), the  $\Delta E_p$  of the redox couple at PMG/GNs–NF/GCE (d) decreased from 110 to 85 mV and a significant enhancement in redox currents for PMG at the PMG/GNs–NF/GCE was achieved. The results indicated that the presence of GNs in PMG/GNs–NF composite film increased the electron transfer rate and improved the performance of electrode. Further addition of *p*-nitrophenol made the anodic peak current of PMG/GNs–NF/GCE (e) to increase, whereas the cathodic peak current decreased concurrently. This behavior showed the PMG/GNs–NF composite film catalyzed the oxidation of *p*-nitrophenol.

In order to further demonstrate the electrocatalytic oxidation of PMG/GNs–NF composite film toward *p*-nitrophenol, the oxidation of *p*-nitrophenol was carried out at bare GCE and PMG/NF–GNs/GCE by linear sweep voltammetry (LSVs). As can be seen in Fig. 2b, direct oxidation of *p*-nitrophenol at bare GCE (a) took place at a considerable overpotential about 0.9 V. Curve b showed the oxidation peak of PMG/NF–GNs composite film in the absence of *p*-nitrophenol. Upon addition of different concentrations of *p*-nitrophenol, new growth in the oxidation peak appeared due to the oxidation of *p*-nitrophenol and the oxidation peak increased with the increase in concentration of *p*-nitrophenol (curves c and d). Compared with bare GCE, the peak current obviously increased and the peak potential negatively shifted. The results confirmed the

PMG/NF–GNs composite film played a significant role in the electrocatalytic oxidation of *p*-nitrophenol.

### 3.3 Optimization of experimental parameters

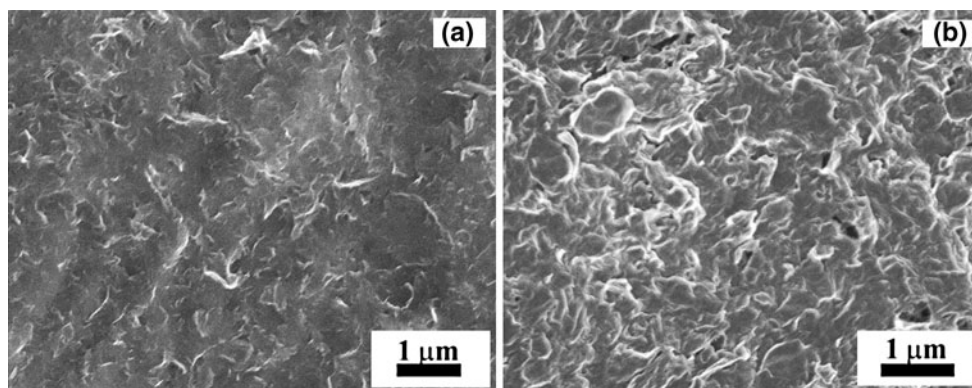
The various experimental parameters affecting *p*-nitrophenol response, the alkaline hydrolysis product of MP, were optimized including pH, accumulation potential, accumulation time, and scanning cycles during polymerization of MG. All the experiments were studied by CVs in 0.1 M PBS in the presence of 0.1 mM *p*-nitrophenol.

The influence of pH on *p*-nitrophenol response was evaluated in the range of 4.0–8.0. As presented in Fig. 3a, the oxidation peak current increased with increasing pH up to 5.0, however, it decreased as pH further increased, which indicated that acid solution was more suitable for the reaction. Thus, a pH 5.0 PBS buffer solution was used in the subsequent experiment.

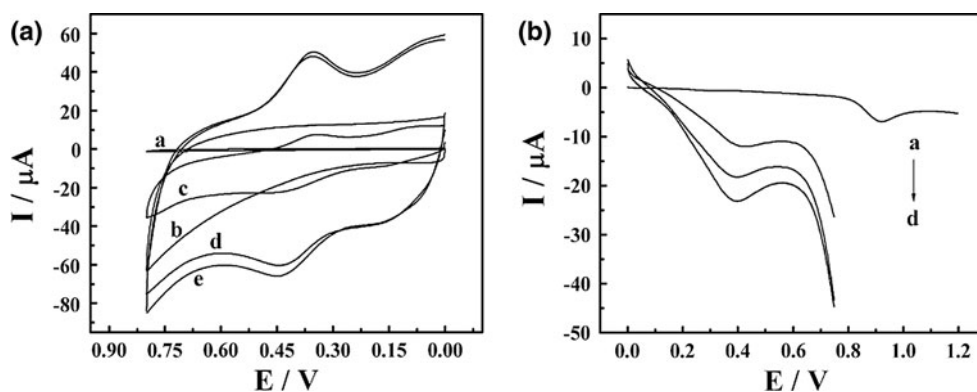
As shown in Fig. 3b, accumulation potential over the range of 0.1–0.6 V was investigated, and the maximum oxidation peak current appeared at 0.3 V. Therefore, the optimal accumulation potential for detection of *p*-nitrophenol was 0.3 V.

The accumulation time dependence of the *p*-nitrophenol response was illustrated in Fig. 3c, with the increase of accumulation time, the oxidation peak current first increased up to a maximum at 150 s and then remained approximate constant, presenting that the accumulation equilibrium was obtained at the electrode/solution interface. Thus, 150 s was selected as the accumulation time in the following investigations.

The thickness of PMG film impacting on the catalytic ability of PMG toward *p*-nitrophenol could be changed by altering scanning cycles during polymerization of MG. The influence of scanning cycles was shown in Fig. 3d, the oxidation peak current first rose and reached a maximum with the 10 cycles and then decreased with a further



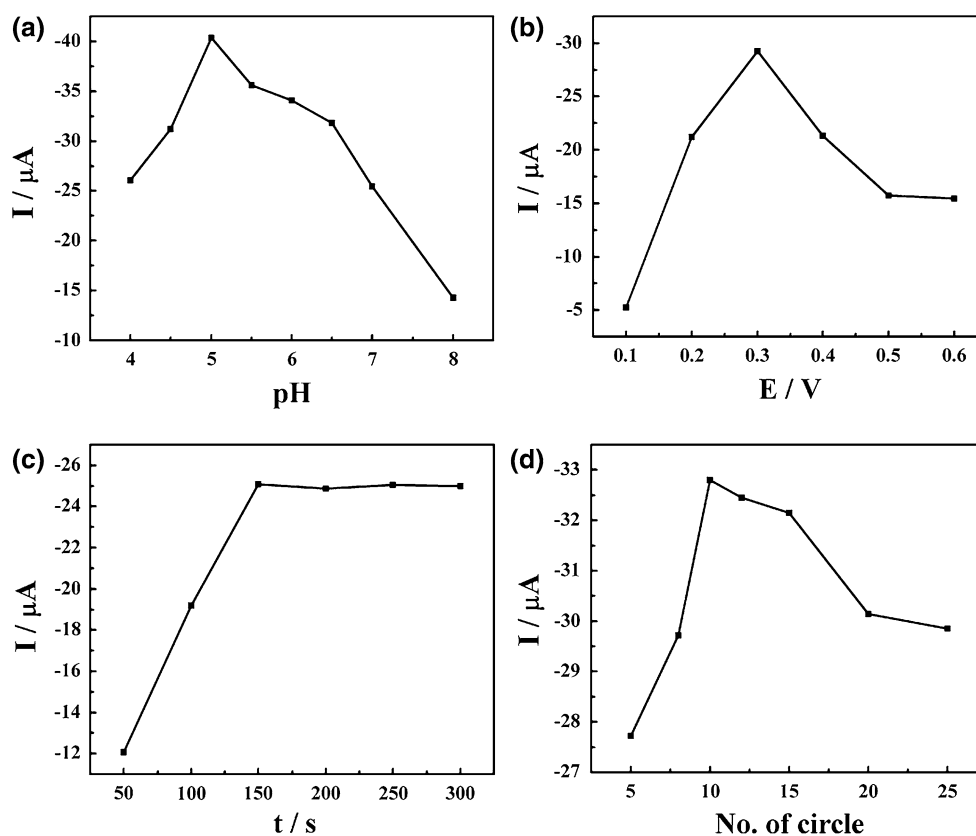
**Fig. 1** SEM images of GNs–NF (a) and PMG/GNs–NF (b) films



**Fig. 2** **a** Cyclic voltammograms of bare GCE (*a*), GNs-NF/GCE (*b*), NF-PMG/GCE (*c*), and PMG/GNs-NF/GCE in the absence (*d*) and presence (*e*) of *p*-nitrophenol in 0.1 M pH 7.0 PBS at a scan rate of  $100 \text{ mV s}^{-1}$ . **b** Linear sweep voltammetry of PMG/GNs-NF/GCE in

0.1 M PBS (pH 7.0) with different concentrations of *p*-nitrophenol: *b* 0, *c* 0.04 mM, *d* 0.08 mM. Curve *a* represents oxidation of 0.1 mM *p*-nitrophenol at bare GCE. Scan rate:  $100 \text{ mV s}^{-1}$

**Fig. 3** Effects of pH (**a**), accumulation potential (**b**), accumulation time (**c**), and scanning cycles during polymerization of malachite green (**d**) on the response of PMG/GNs-NF/GCE to 0.1 mM *p*-nitrophenol in 0.1 M PBS. Scan rate:  $100 \text{ mV s}^{-1}$



increase of cycle number, which may be due to the resistance of PMG film increased with its thickness [21]. To keep the stability and sensitivity of the sensor, the number of 10 scanning cycles was chosen as the operating condition.

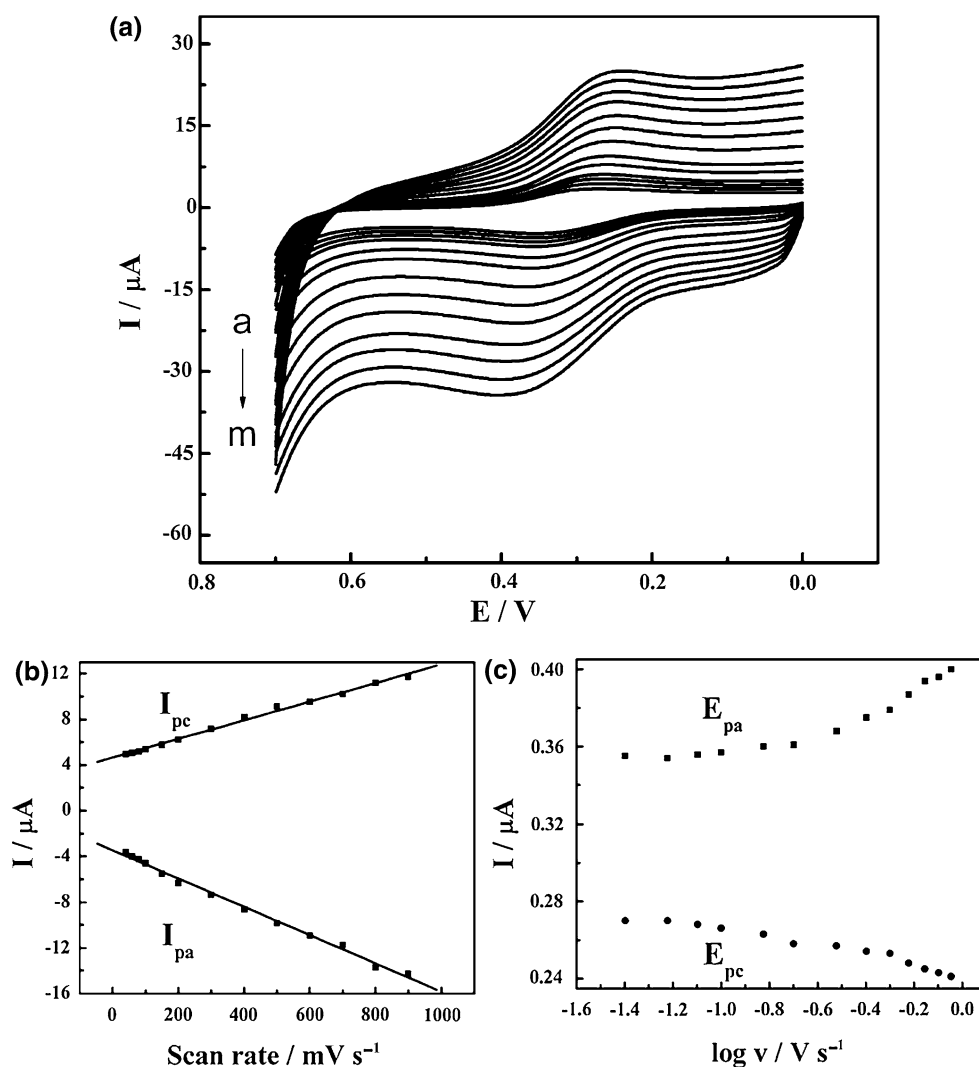
### 3.4 Direct electrochemistry of the modified electrode

The influence of scan rate on CVs performance of the modified electrodes was investigated. Figure 4 showed the

influence of scan rate on CVs performance of PMG/GNs-NF modified electrode in 0.1 M PBS (pH 5.0). As is clear from Fig. 4a, with increasing scan rate, the redox peak currents of PMG film rose slightly. The oxidation peak shifted to more positive potentials, while the reduction peak shifted to more negative potentials with the increase of scan rate, which resulted in the increase of  $\Delta E_p$ . From Fig. 4b, the oxidation and reduction peak currents rose linearly with the scan rate from 0.04 to  $0.9 \text{ V s}^{-1}$ , and the linear regression equations are listed as follows:  $i_{pc} = 0.00814 v + 4.6661$



**Fig. 4** **a** Cyclic voltammograms of the PMG/GNs–NF/GCE in 0.1 M PBS (pH 5.0) at different scan rates: from *a* to *m* are 40, 60, 80, 100, 150, 200, 300, 400, 500, 600, 700, 800 and 900  $\text{mV s}^{-1}$ , respectively. **b** The plots of anodic and cathodic peak current versus scan rate. **c** The relationship of peak potential ( $E_p$ ) versus the logarithm of scan rate ( $\log v$ )



( $\mu\text{A}$ ,  $\text{mV s}^{-1}$ ,  $R = 0.9974$ );  $i_{pc} = -0.01239 v - 3.4480$  ( $\mu\text{A}$ ,  $\text{mV s}^{-1}$ ,  $R = 0.9973$ ), indicating that the reaction is a quasi-reversible surface-controlled process, and verifying MG was stably polymerized on the electrode surface.

In Fig. 4c, plots of  $E_{pa}$  and  $E_{pc}$  versus the logarithm of scan rate produced two straight lines when  $v > 0.5 \text{ V s}^{-1}$ , with slopes of  $2.3 RT/(1 - \alpha)nF$  and  $-2.3 RT/\alpha nF$  based on Laviron's formula [37].

$$\log k_s = \alpha \log(1 - \alpha) + (1 - \alpha) \log \alpha - \log \frac{RT}{nFv} - \frac{\alpha(1 - \alpha)nF\Delta E_p}{2.3RT} \quad (1)$$

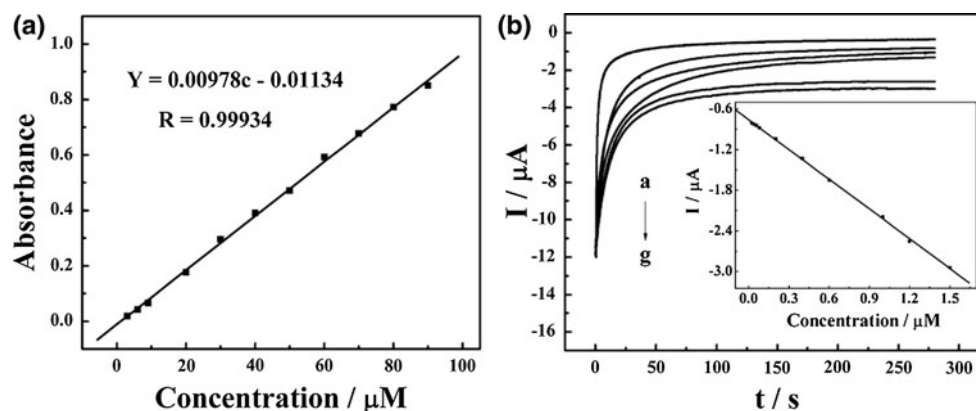
where  $\alpha$  is the electron transfer coefficient,  $n$  is the number of electron, and  $R$ ,  $T$  and  $F$  have their usual meanings ( $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $T = 298 \text{ K}$ , and  $F = 96480 \text{ C mol}^{-1}$ ). According to Eq. (1), the charge transfer coefficient  $\alpha$  was estimated to be 0.64 from the slopes, and the average electron transfer rate constant ( $k_s$ ) was calculated to be  $0.36 \text{ s}^{-1}$ . This  $k_s$  value was higher than that of PMG/NF

( $0.11 \text{ s}^{-1}$ ). From the  $k_s$  values, the increase in ability of electron transfer between the electrode surface and PMG in the presence of GNs is about 327 %. The result indicated a relatively fast electrode reaction process.

### 3.5 Analytical performance

The alkaline hydrolysis conditions including hydrolysis time and the concentration of NaOH were obtained based on the standard curve between *p*-nitrophenol concentration and absorbance (Fig. 5a). Under the optimum hydrolysis conditions, the MP could be completely hydrolyzed to *p*-nitrophenol, which was demonstrated by UV–Vis spectra (shown in Fig. S1, Supplementary Material). 1 M NaOH was added into the MP solution, and the solution was kept at room temperature for 15 min until it was completely hydrolyzed and then followed by the addition of hydrochloric acid to adjust the pH. Then solution was diluted to different concentrations and determined at the

**Fig. 5** **a** Chronoamperometric measurements for a range of *p*-nitrophenol. *a–g* 0, 0.02, 0.2, 0.4, 1.2 and 1.5  $\mu\text{M}$ . **b** The linear relationship between chronoamperometric response current and *p*-nitrophenol concentration



**Table 1** Comparison of various performances of different methyl parathion sensors

Method	Linear range ( $\mu\text{M}$ )	Detection limit ( $\mu\text{M}$ )	References
Au/nafion/GCE	0.5–120	0.1	[36]
Acetylene black-chitosan/GCE	0.02–100	0.002	[38]
MPDE <sup>a</sup> -CdTe QDs/Cys <sup>b</sup> /Au <sub>nano</sub> /MWCNT/GCE	0.019–0.76 0.76–3.8	0.0038	[39]
ZrO <sub>2</sub> /CPE <sup>c</sup>	0.019–11	0.0076	[40]
Gemini surfactant-intercalated clay/GCE	0.4–8.5	0.07	[41]
PMG/GNs-NF/GCE	0.02–1.5	0.002	This work

<sup>a</sup> Methyl parathion degrading enzyme

<sup>b</sup> Cysteamine

<sup>c</sup> Carbon paste electrode

PMG/GNs–NF/GCE by chronoamperometry in 0.1 M PBS (pH 5.0). Figure 5b displayed chronoamperometric responses of various concentrations of MP under the optimum experimental conditions at the PMG/GNs–NF/GCE. As shown in the inset of Fig. 5b, an increase in concentration of MP produced a linear increase in the currents over the range of 0.02–1.5  $\mu\text{M}$ , with the regression equation of  $I_{\text{pa}} (\mu\text{A}) = -1.4597c (\mu\text{M}) - 0.7625$  and the correlation coefficient of 0.997. This proposed method gave the detection limit of 2 nM with  $S/N = 3$ , which was obviously lower than most given in Table 1.

### 3.6 Stability and reproducibility

The stability of PMG/GNs–NF/GCE has also been studied. The potential and peak current of the PMG/GNs–NF-modified electrode remained almost constant after more than 50 CVs in 0.1 M PBS (pH 5.0) over the potential range from 0 to 0.7 V at a scan rate of 100  $\text{mV s}^{-1}$ . According to the equation shown in the previous report [42], the degradation percentages for PMG/GNs–NF and

**Table 2** Determination results of methyl parathion in real samples ( $n = 5$ )

Samples	Added ( $\mu\text{M}$ )	Found ( $\mu\text{M}$ )	Recovery (%)	R.S.D. (%)
Cabbage	1.698	1.775	104.53	4.3
Nai river	0.714	0.708	99.16	2.4
Tap water	0.0357	0.0347	97.20	3.3

PMG/NF were examined to be 10 and 45 % after 100 CVs, respectively (data not shown). These results illustrated that the presence of GNs enhanced the stability of PMG, and the PMG/GNs–NF-modified electrode had a good stability. What is more, the relative standard deviation of the peak currents tested on five modified electrodes with the same treatment was only 3.8 %, indicating that the PMG/GNs–NF-modified electrode is of good reproducibility.

### 3.7 Real sample analysis

In order to further evaluate the practicality of the proposed method, standard addition method was adopted to estimate the accuracy. The UV–Vis spectra of the real samples after hydrolysis have been supplied in the supplementary material (shown in Fig. S2). The recoveries in real samples of vegetable and water were investigated, and the results were summarized in Table 2 with recoveries from 97.20 to 104.53 %. The results indicated that the proposed method was suitable and efficient for the detection of MP in real samples.

## 4 Conclusions

In this study, the PMG/GNs–NF composite film was developed for the detection of MP after being absolutely hydrolyzed to its phenolic derivative in alkaline aqueous solutions. The composite film combining the advantages of easy fabrication, sufficient stability, and good reproducibility had excellent electrocatalysis toward *p*-nitrophenol.

In the composite film, GNs enhanced the electron transfer and stability of PMG. The sensor showed good response with a wide linear range and a low-detection limit. What is more, the application of this PMG/GNs–NF composite film in analysis of real samples was also evaluated with good performance. This proposed method was a promising electrochemical approach for tracing MP.

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